ANNUAL REPORT OF THE ACTING DIRECTOR OF THE FIXED NITROGEN RESEARCH LABORATORY FOR THE FISCAL YEAR ENDED JUNE 30, 1922.

United States Department of Agriculture,
Fixed Nitrogen Research Laboratory,
Washington, D. C., September 14, 1922.

Sir: I have the honor to transmit herewith a report of the work of the Fixed Nitrogen Research Laboratory for the fiscal year ended June 30, 1922.

Since this is the first year the laboratory has been under the Department of Agriculture, it appeared desirable to preface the report by a very brief statement as to the establishment and previous work of the laboratory.

The work of the year was completed under the directorship of Dr. Richard C. Tolman, but his resignation and departure for California, coupled with my unfamiliarity as yet with the details of the organization, has necessitated the preparation of this report by those in charge of the various divisions of the laboratory work with very little assistance from me. For editing this combined material into essentially the form in which it now stands, I am indebted to Dr. J. M. Braham, chief of the cyanamide and utilization section.

Respectfully,

F. G. Cottrell,
Acting Director.

Hon. H. C. Wallace,
Secretary of Agriculture.

ESTABLISHMENT OF LABORATORY.

The problem of nitrogen fixation is one of vital national importance, both in war and peace, since nitrogen forms an essential constituent of explosives, of fertilizers, of dyestuffs, and of many other substances used in the arts. The dependence of the United States on foreign sources for its supply of nitrogen compounds, particularly for the manufacture of explosives, was forcibly brought out during the World War, and the danger in such a policy became clearly evident. The demand for explosives was immensely increased upon the entry of the United States into the war. While attempts were made to meet the immediate requirements by importation of nitrates from Chile and by the stimulation of domestic production,

principally by-product coke-oven ammonia, the War Department turned to the fixation of atmospheric nitrogen as a means of securing an adequate supply of explosives. Unfortunately, the country was unprepared to solve this problem quickly, due to the lack of the highly technical information and experience required in nitrogen fixation and in the transformation of nitrogen compounds. Although much progress in the relatively new art of nitrogen fixation was made in this country during the latter period of the war, the imperative necessity for further research on nitrogen fixation had been clearly shown.

The Fixed Nitrogen Research Laboratory was established by the Secretary of War on March 29, 1919, for the purpose of continuing the various researches on nitrogen fixation initiated during the war, to obtain further information necessary for the peace-time utilization of the two nitrate plants constructed by the Government at Sheffield and Muscle Shoals, Ala., and to conduct such other investigations as would further the problem of economically producing nitrogen compounds. Authority for this work is contained in the national defense act of June 3, 1916 (subsection "Nitrate plants"), specifically authorizing the President to "cause to be made such investigations as in his judgment are necessary to determine the best, cheapest, and most available means for the production of nitrates and other products for munitions of war, and useful in the manufacture of fertilizer and other products." Funds for the prosecution of the work are obtained from an appropriation made under this act.

On July 1, 1921, the laboratory was transferred by Executive order from the War Department to the United States Department of Agriculture, in view of the fact that nitrogen fixation is largely an agricultural problem in peace times. The laboratory is located at American University, Washington, D. C., making use of buildings and equipment formerly used by the Research Division, Chemical Warfare Service, United States Army. It has a total personnel of 108, exclusive of its consulting staff of chemists and engineers. The authorized expenditure for the fiscal year ended June 30, 1922, was $250,000; the actual expenditure was $241,011.70.

PREVIOUS WORK OF THE LABORATORY.

The early work of the laboratory was carried out with particular reference to the peace-time utilization of the two Government-owned nitrate plants in Alabama. The cyanamide plant at Muscle Shoals (known as United States nitrate plant No. 2) is the largest cyanamide plant in the world, having a capacity of 220,000 tons of cyanamide or 110,000 tons of ammonium nitrate per annum. This plant operated very successfully in the test run which was made shortly after the signing of the armistice. The principal work, therefore, which the laboratory has carried out in connection with the peace-time utilization of this plant has been to consider what products of fertilizer value could be made there, since it is evident that such a large quantity of fixed nitrogen can be utilized only for agricultural purposes.

The nitrate plant at Sheffield (known as United States nitrate plant No. 1) was designed to operate by the direct synthetic (or Haber) process, with a capacity approximately one-fifth that of

the cyanamide plant, or 22,000 tons of ammonium nitrate per annum. The plant in its original form was not a success, however, due in part to insufficient technical information on the various physical-chemical steps which go to make up the process. The laboratory, therefore, undertook investigations to supply such technical information.

In addition to research carried out in connection with these two projects, the laboratory has conducted investigations on other methods of nitrogen fixation, as well as on the transformation and utilization of nitrogen compounds.

The principal results of the investigations made by the laboratory up to the time of its transfer, July 1, 1921, are described in 76 technical reports made to the Chief of Army Ordnance. Some of the material has already been published in scientific and technical journals. In the future it is planned to publish such technical information as will be of interest to the nitrogen industry as a whole. The main accomplishments of the laboratory to November, 1921, are described in a recently published report on the "Fixation and Utilization of Nitrogen" prepared by the nitrate division, Ordnance Office, War Department, assisted by this laboratory.

WORK OF THE LABORATORY FOR THE FISCAL YEAR ENDED JUNE 30, 1922.

The work of the Fixed Nitrogen Research Laboratory during the fiscal year ended June 30, 1922, has been in part an extension of the investigations already referred to and in part a study of new problems. Seventeen technical reports on the work of the laboratory were prepared during the past year. The main lines of investigation conducted during this period and the more important results are briefly summarized in the following:

INVESTIGATIONS ON FIXATION PROCESSES.

At the present there are essentially three processes for the fixation of atmospheric nitrogen in commercial operation in various parts of the world. These are known as the direct synthetic ammonia (or Haber) process, the cyanamide process, and the arc process. Several others, such as the alkali cyanide (Bücher), the aluminum nitride (Serpek), and the explosion (Häuser) processes, have also been investigated on a fairly large scale of operation in several countries, but as yet can not be considered as commercially established in the sense of the other three.

In the present state of development of fixation processes in this country, fixed nitrogen can not be produced for fertilizer purposes in competition with Chilean nitrate and with ammonia obtained as a by-product in the coking of coal, except under unusually favorable circumstances. There is every reason to believe, however, that the cost of fixation can be materially reduced through further study and development. During the past year the laboratory has studied the cyanamide, synthetic ammonia, arc, and alkali cyanide processes with that object in view.

DIRECT SYNTHETIC AMMONIA PROCESS.

The direct synthetic ammonia process is the newest of the three commercially developed processes and is the one which at present apparently offers the greatest opportunity for further development. The laboratory has therefore carried on a large amount of work in connection with it during the past year. In this process a purified mixture of nitrogen and hydrogen is subjected to a very high pressure and passed over a suitable catalyst maintained at about 500° C. Under these conditions nitrogen and hydrogen combine chemically to form ammonia to the extent of from 5 to 15 per cent of the gases present, the percentage depending on the catalyst and operating conditions. The ammonia thus formed is removed and the uncombined gases returned to the apparatus and again treated.

The main features of this process which require further development and on which the laboratory has been engaged during the past year are: The catalyst problem, involving the large-scale production of an active catalyst, the further development of the present catalyst, and the search for new and improved catalysts; the production and purification of the hydrogen-nitrogen mixture; the development of apparatus which will stand the unusually high pressures and temperatures used; and the removal of the synthesized ammonia from the unconverted gas.

The catalyst for effecting the union of nitrogen and hydrogen is in a sense the heart of the direct synthetic ammonia process. The efficiency of the catalyst is in general very greatly reduced by even exceedingly small amounts of impurities in the gas mixture passing through it, hence the necessity of pure gas. The laboratory has continued its studies on the development of a catalyst which will be more active and less affected by impurities than those previously used. The laboratory has developed a satisfactory ammonia catalyst and has perfected a method for its large-scale production. This is a particularly important advance in the development of the synthetic ammonia process. Research on the theory of catalytic action was continued throughout the year, since the art of catalyst manufacture can be placed on a firm scientific basis only through a thorough knowledge of catalytic action.

The production of hydrogen of required purity constitutes the main cost of the entire process, the cost of nitrogen being relatively small. The production and purification of hydrogen from various commercial sources have been studied and improvements in the method of purifying the gas have been made. The laboratory has given special attention to the utilization of waste hydrogen for the synthesis of ammonia. Such waste hydrogen now occurs in connection with the electrolytic manufacture of bleaching materials, caustic alkali, and oxygen. The individual amounts to be considered vary over a range of 20,000 to 100,000 cubic feet per day at the different plants, but the total amount going to waste in America is large enough to be a factor of importance. For the utilization of these relatively small quantities of waste hydrogen, methods of operation quite different from those in large installations must be considered, since some of the economies which can be introduced by large-scale installations are not possible in this case. The laboratory has developed and installed apparatus particularly adapted to the syn-

thesis of ammonia, using waste hydrogen. This equipment has been in continuous operation for several months and important information on the various steps of the process was obtained. This work, when completed, will provide the information necessary for the installation and operation of small ammonia plants throughout the country.

In connection with the engineering features of the process, the construction of a synthetic ammonia plant on a semicommercial scale was begun, so that the numerous mechanical problems involved can be better studied. The plant will also afford a means of testing catalysts under conditions more closely approximating those in commercial operation.

Another problem of great importance and considerable complexity is that of obtaining a material suitable for the construction of the catalyst chambers in which the reaction between nitrogen and hydrogen to form ammonia takes place. Ordinary carbon steel can not be employed, since it rapidly deteriorates, becoming porous and in many cases so brittle that it can be broken with the fingers. To obtain reliable information on this problem, the laboratory has had under test 25 bombs made from different materials. Although the test is still in progress, very important information as to suitable materials for construction of catalyst chambers has already been obtained.

The design and development of apparatus to operate at very much higher pressure than is now regarded as commercially feasible was also undertaken, since ammonia formation is greatly favored by increasing pressure. Although this problem is quite beyond the range of present engineering experience, satisfactory progress was made and important developments along this line are to be expected.

The removal of ammonia from the gas mixture after its passage through the catalyst is a problem of considerable importance in this process. The difficulty lies in removing practically all of the ammonia from the mixture, of which it forms about 5 to 15 per cent, without introducing impurities in the gases which are harmful to the catalyst. The Bureau of Soils, in cooperation with this laboratory, has studied various methods of effecting the removal, and has developed a promising method based on scrubbing the gas under high pressure with a relatively concentrated solution of ammonia, recovering the ammonia thus removed by releasing the pressure on the solution, and liquefying the liberated gas by compression.

The laboratory has published during the past year eight articles in Chemical and Metallurgical Engineering and in the Journal of the American Chemical Society on various phases of the work on the direct synthetic ammonia problem.

CYANAMIDE PROCESS.

In the cyanamide process of nitrogen fixation, calcium carbide is first produced by fusing a mixture of coke and lime in an electric furnace. The carbide is then powdered, heated to a high temperature, and subjected to the action of nitrogen, usually obtained by fractional distillation of liquid air, with which it combines to form a solid compound, calcium cyanamide. The nitrogen thus fixed can be transformed into a great variety of nitrogen compounds. The

process has been in commercial operation much longer than the synthetic ammonia process, and consequently is in a much higher state of development.

The laboratory has made a rather critical study of the present form of the process, from which it appears that improvements leading to a drastic reduction in the cost of operation are rather improbable. The process requires a relatively large amount of electric power for the manufacture of carbide, and hence cheap power is necessary to its profitable operation. Since the manufacture of carbide is now a standardized process, the possibility of materially reducing the power requirements seems somewhat remote. The nitrification of carbide, the second step in the process, is about 85 per cent efficient in the best commercial practice and hence offers some opportunity for improvement. During the past year experimental studies have been undertaken on the fundamental reactions involved in this process for the purpose of determining how improvements might be advantageously made in the present form of the process, as well as to obtain data which may suggest a modification leading to a reduction in cost of operation. Important data on the formation and decomposition of cyanamide have already been obtained, but further study is required to complete the investigation. Researches of this character, as well as those mentioned later in connection with the cyanide process, should throw much light on the reactions of free nitrogen to form cyanamide, cyanides, and nitrides.

ARC PROCESS.

The arc process is the oldest and, in many respects, the simplest of the three commercially developed methods of nitrogen fixation. It has the very important advantages from a military standpoint that it can be rapidly installed in case of war, and that it provides nitrogen directly in the nitrate form. Since the Government does not own an arc plant, the laboratory has given much less attention to this process, for the time being, than to the other processes. The experimental studies have been confined largely to the fundamental theory of chemical reactions in the path of the electric discharge.

During the past year the laboratory made a rather critical survey of the present form of the process, with a view of ascertaining the nature and extent of the improvements which can be made. The results of this study are given in the "Report on the fixation and utilization of nitrogen." The study showed, in particular, the necessity of improving the method of nitrogen-oxide recovery and of increasing the efficiency of furnace operation. Experimental studies made in connection with nitrogen-oxide recovery are briefly described in a later section of this report. To materially increase the energy efficiency of the process, which at the present time is very low, a more accurate knowledge of the reactions occurring in various types of electric discharge is absolutely essential. In this connection a study was made of the production of ozone by the corona discharge and the production of active nitrogen in the low-pressure arc and in an electrodeless discharge. A number of physical and chemical properties of these two highly interesting and important substances were also determined. Investigations of reactions in the path of

electric discharges are continuing, for there is reason to believe that very fundamental improvements may be achieved through such studies.

CYANIDE PROCESS.

As previously mentioned, the cyanide process of nitrogen fixation has not been successfully developed on a commercial scale. The form of the process developed in this country consists essentially of heating a mixture of soda ash, carbon, and iron to an elevated temperature in the presence of nitrogen gas. The product is a crude cyanide containing 5 to 10 per cent nitrogen which can either be treated to produce a marketable form of cyanide or subjected to the action of steam to produce ammonia. Several important advantages are claimed for the process and much experimental work has been done on it in this country. During the war the Government built a plant for the production of cyanide at Saltville, Va., which was designed to have a capacity of 10 tons of cyanide per day. Although some cyanide was produced, it was shown during the short period of operation that both the chemical and engineering features of the process required further study and development.

The laboratory has made a general survey of this process, the results of which are published in the report on the fixation and utilization of nitrogen. It became evident that two types of research were necessary to its further development—research which would afford a more accurate knowledge of the fundamental reactions involved in sodium cyanide formation, and research on the engineering features of the process, particularly the development of a satisfactory method of manipulating the charge under treatment. The laboratory has been conducting research of the first type. A study was undertaken to determine the influence of such factors as quality and proportions of materials, temperature and duration of treatment, purity of nitrogen, and presence of iron, on the completeness and rate of cyanide formation. The results already obtained indicate that failure to obtain satisfactory conversion to cyanide in the semicommercial tests which have been made in the past was due in part to the low quality of carbon and iron used. Information on the mechanism of the reaction has also been obtained, which suggests ways of improving the process. The work on this process is continuing.

There is some doubt as to whether the cyanide process can be so developed that fertilizer can be produced as cheaply by it as by other processes. It should be pointed out, however, that the development of a process for the production of cyanide, as a final product, directly from atmospheric nitrogen, is very important in view of the increasing demand for nitrogen in the form of cyanides. Until recently their large-scale commercial use was confined essentially to the hydrometallurgy of gold and silver ores, with smaller quantities consumed in casehardening and electroplating, but in recent years the application of hydrocyanic acid as a fumigating agent for fruit trees has opened a new and rapidly growing market of particular interest to this department.

INVESTIGATIONS ON THE TRANSFORMATION AND UTILIZATION OF NITROGEN COMPOUNDS.

Next in importance to the fixation of nitrogen is the transformation of the different nitrogen-containing substances in order to make them more useful in agriculture, in explosives, and in the arts. During the past year the laboratory has conducted a number of investigations in this connection. Since many of them are described in the report on the fixation and utilization of nitrogen, only the more important ones will be referred to in this report.

SYNTHESIS OF UREA.

Urea is one of the most attractive nitrogen-containing materials from the fertilizer standpoint, but at the present time its cost for such use is prohibitive. The laboratory has developed on a semitechnical scale a process for the production of urea from ammonia and carbon dioxide which seems to possess possibilities of ultimately yielding this material at fertilizer prices. The process could be very advantageously operated in conjunction with a direct synthetic ammonia plant employing the water-gas reaction for hydrogen, since waste carbon dioxide would in that case be available. The results of the investigation on this process were published in the July, 1922, issue of the Journal of Industrial and Engineering Chemistry.

OXIDES OF NITROGEN.

Oxides of nitrogen are obtained as the direct product in the arc process of nitrogen fixation, in the conversion of ammonia nitrogen to nitrate nitrogen by oxidation, and also in various nitration processes. At the present time the recovery of oxides of nitrogen from the dilute gas mixtures obtained in all these processes requires very large and expensive absorption systems. Furthermore, the product is a dilute acid, the further concentration of which is also expensive. The importance of developing a process by which the final product can be directly obtained in suitable form, particularly as concentrated nitric acid and dry nitrogen tetroxide, is therefore evident.

The laboratory has made considerable progress in the solution of this problem during the past year. The two main phases of this problem are the separation of the oxides of nitrogen from the accompanying gas and the conversion of the concentrated gases thus obtained into concentrated nitric acid. The utility of silica gel in effecting the separation as well as for the production of dry nitrogen tetroxide has been shown, but further work is required to determine the optimum conditions of operation of this new process. Work was also begun on the direct production of concentrated nitric acid from concentrated oxides of nitrogen. In connection with the possibility of producing concentrated or fuming nitric acid from extremely dilute oxides of nitrogen, so dilute that they are now wasted, a careful study of the reaction between ozone and nitrogen tetroxide was made. It was found that the conversion to nitrogen pentoxide is rapid and quantitative. The present high cost of producing ozone, however, is a limiting factor in commercially applying this process.

CYANAMIDE.

The direct product of the cyanamide process of nitrogen fixation is calcium cyanamide. From this compound an extremely wide variety of products is obtainable. Thus, in addition to cyanamide, there may be obtained by transformation processes ammonia, nitric acid (by ammonia oxidation), cyanides, hydrocyanic acid, cyanamide, dicyanodiamide, urea, guanylurea, guanidine, etc., and the numerous derivatives of these latter compounds which are becoming important in the manufacture of dyes, drugs, and explosives. Many of these important compounds can not be furnished in quantity by any other process.

The laboratory is making a rather extensive study of the chemistry of cyanamide and its derivatives to open up this new and cheap source of numerous, useful compounds. During the past year methods have been developed for the production of free cyanamide (H_2CN_2) in quantity, for the production of urea from cyanamide on a semitechnical scale, and for the preparation of guanidine salts. Cyanamide derivatives which appear to have value as ingredients in explosives have also been studied and the results of the investigations communicated to the ammunition division, Ordnance Office, War Department. In addition, a theoretical investigation on the chemistry of cyanamide was made for the purpose of clarifying the chemistry of this large group of compounds. This investigation is being continued.

AGRICULTURAL UTILIZATION OF FIXED-NITROGEN COMPOUNDS.

Very little information was available as to the agricultural value of many of the new compounds which are now produced by nitrogen fixation. In view of the possibility of operation of the Government nitrate plants in the then near future, fertilizer experiments were begun at Muscle Shoals and Sheffield, Ala., in 1919, in cooperation with the Bureau of Plant Industry of the department. These experiments were continued by the laboratory to the end of the 1921 season, when they were discontinued. An area of about 20 acres, divided into nearly 500 plots, was used for these experiments, and the following nitrogen materials were tested, chiefly on cotton and corn: Commercial cyanamide, ammonium nitrate, ammonium chloride, ammonium phosphate, ammoniated superphosphate, double salt consisting of ammonium nitrate and ammonium sulphate, chloride mixed salt (made from ammonium nitrate and potassium chloride), sulphate mixed salt (made from ammonium nitrate and potassium sulphate), urea, calcium nitrate, and mixtures of calcium nitrate and cyanamide in various proportions. Sodium nitrate and ammonium sulphate served as standards for comparison. The results of these investigations are now being prepared for publication.

Samples of a number of the above compounds have been prepared for agricultural tests made by the soil fertility investigations section and the tobacco investigations section, Bureau of Plant Industry, at their various experimental fields. In addition, pot experiments have been carried out in cooperation with the soil fertility investigations section to determine the effect on plant growth of numerous other

nitrogen compounds, particularly derivatives of cyanamide. Chemical and biological studies have also been made on the transformations of cyanamide in the soil.

In connection with the utilization of commercial cyanamide as a fertilizer, the following investigations were completed during the past year: The stability of cyanamide on storage, the reactions which limit the use of cyanamide in fertilizer mixtures containing acid phosphate, and the possibility of utilizing cyamamide in admixture with calcined phosphate. The results of these studies are now being prepared for publication.

It is evident from the foregoing outline of the work and accomplishments of the laboratory that the field of nitrogen fixation and utilization is an exceedingly large one. Thus, improvement in the existing processes of nitrogen fixation, the investigation of proposed but untried processes, the discovery and development of entirely new processes, and the investigation and transformation of nitrogen compounds to make them most useful, present almost limitless possibilities for fruitful research.

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